

ASTM E 1559 METHOD FOR MEASURING MATERIAL OUTGASSING/DEPOSITION KINETICS HAS APPLICATIONS TO AEROSPACE, ELECTRONICS, AND SEMICONDUCTOR INDUSTRIES

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ABSTRACT

The American Society for Testing and Materials has published a new standard test method for characterizing time and temperature-dependence of material outgassing kinetics and the deposition kinetics of outgassed species on surfaces at various temperatures. This new ASTM standard, E 1559¹, uses the quartz crystal microbalance (QCM) collection measurement approach. The test method was originally developed under a program sponsored by the United States Air Force Materials Laboratory (AFML) to create a standard test method for obtaining outgassing and deposition kinetics data for spacecraft materials. Standardization by ASTM recognizes that the method has applications beyond aerospace. In particular, the method will provide data of use to the electronics, semiconductor, and high vacuum industries.

In ASTM E 1559 the material sample is held in vacuum in a temperature-controlled effusion cell, while its outgassing flux impinges on several QCMs which view the orifice of the effusion cell. Sample isothermal total mass loss (TML) is measured as a function of time from the mass collected on one of the QCMs which is cooled by liquid nitrogen, and the view factor from this QCM to the cell. The amount of outgassed volatile condensable material (VCM) on surfaces at higher temperatures is measured as a function of time during the isothermal outgassing test by controlling the temperatures of the remaining QCMs to selected values. The VCM on surfaces at temperatures in between those of the collector QCMs is determined at the end of the isothermal test by heating the QCMs at a controlled rate and measuring the mass loss from the QCMs as a function of time and temperature. This reevaporation of the deposit collected on the QCMs is referred to as QCM thermogravimetric analysis. Isothermal outgassing and deposition rates can be determined by differentiating the isothermal TML and VCM data, respectively, while the evaporation rates of the species can be obtained as a function of temperature by differentiating the QCM thermogravimetric analysis data.

This paper describes the ASTM E 1559 test method and presents some typical data. The paper also describes the Lockheed ASTM E 1559 test apparatus.

INTRODUCTION

Up to the present time two material screening techniques have been used by the aerospace and microelectronics industries, ASTM E 595² and ASTM F 1227³, respectively, to measure total mass loss (TML) and collected volatile condensable materials (CVCM). These standards both specify single sample and deposition surface temperatures, and a single test duration, and provide integral rather than time-dependent TML and CVCM data. The vacuum/space compatibility of a material is determined by comparing its TML and CVCM data with arbitrary criteria. While the data measured by the ASTM E 595 and ASTM F 1227 tests are very valuable for material comparison and screening, they do not reflect the impact of a material on the performance of a specific component or system, with specific material and deposition surface temperatures.

In order to accurately predict the impact of contamination on space system performance, the aerospace community customarily models contamination generation, migration, and deposition using computer codes to represent the geometry and operational temperatures of the system of interest. This type of system modeling requires as input time- and temperature-dependent material outgassing/deposition kinetics data, which cannot be generated by the previous ASTM test methods. The Air Force Materials Laboratory Non-Metallic Materials Group recognized this situation and initiated a program with Lockheed Missiles & Space Company to develop a standardized method for characterizing materials outgassing rates and deposition kinetics. Between 1982 and 1989 Lockheed verified a test approach, designed a suitable test apparatus and developed the test procedure. This test method was demonstrated by establishing a twenty-material database for the Air Force, and by supporting numerous Lockheed and out-of-house programs with material outgassing measurements. A full description of the Air Force program and the test method developed is presented in the contract final report ⁴. After the successful completion of this contract, the Air Force solicited the support of the ASTM Subcommittee E21.05 to pursue incorporation of the Lockheed developed method as a new ASTM standard test. The current edition of this standard was approved August 15, 1993 and is designated ASTM E 1559.

This paper describes the basic QCM collection measurement approach and reviews the major features of the ASTM E 1559 test method. The standard specifies certain apparatus minimum performance requirements and key dimensions, but much of the vacuum system and data acquisition system design can be chosen by the user. The paper therefore describes ASTM E 1559 apparatus requirements using the current Lockheed apparatus as an example. The paper also presents examples of the type of data provided by the test.

TEST METHOD

The QCM Collection Measurement Method

The QCM collection method for measuring outgassing and deposition kinetics is shown schematically in Figure 1. The material sample is placed in a temperature-controlled effusion cell in a vacuum chamber. Outgassing flux leaving the effusion cell orifice impinges on several QCMs which are controlled at selected temperatures. One of the QCMs is cryocooled, usually by liquid nitrogen for reasons of practicality, so as to collect essentially all the impinging species. The sample percent total mass loss (TML) and outgassing rate from the sample are determined as functions of time from the mass deposited on this QCM and the cell orifice-to-QCM view factor. The percent of outgassing species which are condensable on higher temperature surfaces is referred to as Volatile Condensable Material (VCM) and is measured as a function of time from the mass collected on the other QCMs, which are temperature-controlled appropriately. The QCMs and effusion cell are surrounded by a liquid nitrogen shroud to ensure that the molecular flux impinging on the QCMs is due only to the sample in the effusion cell.

After the isothermal outgassing test, a QCM thermogravimetric analysis (QTGA) is performed on the condensed outgassed species. The QCMs are individually heated at a controlled rate from their base temperatures to 398 K in order to volatilize the collected species, while the mass remaining on the QCMs is measured as a function of time and temperature. In general, the collected species have different evaporation characteristics and hence will leave the QCM surface at different temperatures. Therefore, QTGA data are characterized by temperature regimes in which the deposit mass remaining on the QCM decreases due to evaporation of a particular species, separated by temperature regimes in which no species evaporate. The number of temperature regimes in which the QCM deposit mass decreases indicates the number of major species present in the outgassing flux. The relative amount of a given species in the outgassing flux can be estimated from the ratio of the mass loss associated with the evaporation of that species to the total deposit mass on the QCM. QTGA also provides an effective means to clean the QCM surfaces before subsequent outgassing tests.

As shown in Figure 1, the QCM collection method allows for an optional mass spectrometer to be installed on the test chamber. By monitoring the mass spectra of the sample outgassing flux during the

isothermal test, and of the evaporation flux from the QCM during QTGA it is possible in many cases to identify the outgassed species, and to determine the relative outgassing rates of the different species.

The major advantages of the QCM collection method are ability to measure both outgassing and deposition data simultaneously; lack of constraints on sample size and shape (as long as it fits inside the effusion cell); and ability to thermally analyze the outgassed species by QTGA. The major possible disadvantages are the indirect nature of the mass measurement; non-condensability of some outgassed species at liquid nitrogen temperature; and possible influence of effusion cell pressure on outgassing rate. The error in mass measurement using calculated QCM/cell view factors has been shown to be no more than ± 2 percent⁴, and can be eliminated entirely by calibrating the apparatus using a material of known vapor pressure. Sample mass loss data obtained by QCM collection with pre- and post-test microbalance weighings have been found to agree within a few percent, confirming that most significant outgassed species are condensable at 90 K. Studies have shown⁴ that effusion cell pressure can be kept low enough to have negligible effects on outgassing rates if the ratio of sample total outgassing rate to effusion cell orifice size is kept below easily maintainable limits.

The ASTM E 1559 Test Method

ASTM E 1559 is based on the QCM collection method described above, with two types of test method constraints - Test Method A and Test Method B. Test Method A uses standard effusion cell temperatures, three QCMs with polished aluminum electrodes at standard temperatures, and apparatus dimensions and geometries in order to give standard view factors from the QCMs to the effusion cell orifice. Test Method B allows for deviations from these parameters in order for the user to perform custom tests using application-specific parameters or a modified apparatus.

Specifications for the ASTM E 1559 Test Standard are based on the design and performance of the vacuum outgassing/deposition kinetics apparatus and test procedure used at Lockheed. These specifications are summarized below. The apparatus in use at Lockheed performs tests under Test Method B in that an optional fourth QCM is used, the QCMs have gold electrodes, and an optional mass spectrometer is also installed.

TEST APPARATUS

The major components of an ASTM E 1559 test apparatus are the vacuum system, the internal outgassing/ deposition measurement configuration, and the data acquisition system.

Vacuum System

The principal components of the vacuum system are the main test chamber, the cryogenic cold shrouds, and the interlock chamber.

Lockheed's main test chamber is a stainless steel cylinder 50 cm high by 30 cm diameter and contains a liquid nitrogen-cooled shroud. This shroud minimizes molecular contamination from sources other than the effusion cell from reaching the QCMs and reduces the radiative heat load on the QCMs. A cryopump is used on the Lockheed chamber to maintain high-vacuum. The test apparatus in use at Lockheed is shown in Figure 2.

The ASTM standard requires that an interlock chamber be provided to permit the effusion cell to be placed in and removed from the main chamber without having to warm up the internal components and repressurize the main chamber. The interlock chamber is connected to the main chamber via a gate valve through which the effusion cell can be passed. Lockheed's interlock chamber uses a turbomolecular and direct-drive mechanical pump to perform the initial evacuation of the sample from atmospheric pressure.

Internal Measurement Configuration

The outgassing/deposition measurement system includes the QCM assembly and the effusion cell. The QCM assembly consists of three QCMs, a cryogenic heat sink for the QCMs, and a system of cooled shrouds. An optional fourth QCM is utilized on the Lockheed system.

The ASTM E 1559 standard requires that the QCMs consist of two crystals (one for mass collection and one for reference) and that they have a sensitivity of at least $1 \times 10^{-8} \text{ g/cm}^2 \text{ Hz}$ at 298 K. This is typically accomplished with crystals that have natural frequencies of 10 MHz to 15 MHz. The QCM crystals should have optically polished (i.e. specular) surfaces with uncoated aluminum electrodes. The Lockheed apparatus uses QCMs with 39°40' AT cut 10 MHz crystals that have a sensitivity of $4.49 \times 10^{-9} \text{ g/cm}^2 \text{ Hz}$. These crystals have optically polished surfaces with gold electrodes. Because of this electrode deviation from the standard, Lockheed stipulates that its apparatus is operating under Test Method B of the ASTM standard.

The QCMs are arranged symmetrically so that the sensing surface of each of the QCMs has the same view factor to the effusion cell orifice. The QCMs are angled at 10° from the vertical so that their axes intersect each other at a point 150 mm from the crystal surfaces. This intersection point is where the effusion cell orifice exit plane is positioned.

The QCM assembly has cryogenic heat sinks to thermally ground the QCMs to $\leq 90 \text{ K}$ and cold shrouds to limit the impinging flux on the QCMs to the line-of-sight from the effusion cell orifice. The Lockheed apparatus utilizes a liquid nitrogen reservoir to obtain the necessary cryogenic temperatures conveniently and inexpensively. The QCMs are heat sunk to the bottom of the liquid nitrogen reservoir and are thermally shielded from each other by copper plates extending downwards between adjacent QCMs. The ASTM standard requires that each QCM have an independent temperature sensing and control system to allow the QCMs to be heated from their cryogenic heat sink temperature to 398 K. The temperature control system must be capable of controlling the QCM temperatures to a precision of $\pm 0.5 \text{ K}$ or better and also be capable of ramping the QCM temperatures at a constant rate of 1 K/minute.

The ASTM effusion cell is a cylindrical container approximately $65 \pm 5 \text{ mm}$ inside diameter by $50 \pm 5 \text{ mm}$ in deep, and is machine from copper or aluminum for high thermal conductivity. Lockheed utilizes a 63 mm diameter by 51 mm deep aluminum cell. The cell has a detachable cover plate which allows for insertion of material samples. This lid has a cylindrical orifice from which the outgassing flux from the sample exits. The orifice dimensions determine the flux distribution and are specified to be $3.0 \pm 0.1 \text{ mm}$ diameter by $3.0 \pm 0.1 \text{ mm}$ long. The cell has an integral temperature sensor and heater, and control system which permits operating the cell from ambient to 398 K with a precision of $\pm 0.5 \text{ K}$ or better. The effusion cell is positioned inside the main test chamber so that the center of the cell orifice exit plane coincides with the intersection point of the QCM axes. The cell orifice thus has the same view factor to the all four QCMs. The cell orifice is $150 \pm 1 \text{ mm}$ from the surface of the sensing crystal in each QCM.

Data Acquisition System

The ASTM standard test method does not specify a particular data acquisition technique. However, frequency and temperature data from the QCMs, temperature data from the effusion cell, and the time of data collection must be acquired at specified intervals over relatively long time periods (perhaps several days for an isothermal outgassing test). An automated computer-based data acquisition system is highly recommended to facilitate raw data recording and subsequent data processing and archiving. Lockheed utilizes a personal computer to control QCM and effusion cell operations and to acquire the necessary data. Data reduction is then readily accomplished by manipulating the data spreadsheet.

Additional Supporting Equipment

An analytical laboratory balance is required for pre- and post-test weighing of material samples. The balance should have a 30 gram or greater tare (since this test method uses rather large samples) and it should have a readability of 10 μ gram or better with a precision of ± 10 μ gram.

Hardware Cleaning

The ASTM standard provides guidelines for vacuum chamber preparation and QCM handling and cleaning. These guidelines are consistent with common high vacuum practices and recommended instructions from QCM vendors.

TEST SAMPLE REQUIREMENTS

ASTM E 1559 was developed to allow outgassing characterization of a wide variety of materials including adhesives, sealants, cable insulation, conformal coatings, electrical components, films and sheet materials, greases and liquids, pre-molded elastomer compounds, and tapes. In general, in order to perform an outgassing measurement, a representative sample of the material need only fit inside the effusion cell. Meaningful data interpretation requires that the material be well described in terms of its preparation, composition, and pre-conditioning. All sample material details pertinent to its heritage including batch or lot numbers should be noted.

Since outgassing of most space materials is diffusion-controlled, the test sample is prepared in either the geometry in which it is to be used, or in a geometry which permits the measured outgassing data to be related to a sample with another geometry using diffusion theory. Sample dimensions are, therefore, critical to data analysis and are measured to an accuracy of ± 1 percent.

ASTM E 1559 specifies sample configurations, sample holders, and allowable geometries for a variety of different types of materials in order to constrain the internal diffusion flow to one dimension or to be representative of the materials application. Examples of the non-outgassing sample holders include 10 mm by 25 mm aluminum tubes for holding adhesives or sealants, and aluminum foil substrates for conformal coatings.

Initial sample mass is determined by the degree of sample outgassing and apparatus/QCM sensitivity limitations. Too small a sample may produce too small a deposit on the QCMs for accurate outgassing characterization and too large a sample may produce a deposit on a QCM large enough to damp the sensing crystal and thus saturate the output signal. Large deposits may also induce non-linear responses from the QCM particularly if the deposit is liquid rather than solid. Experience has shown that sample sizes of 0.5 to 10 gram (not including any substrate) consistently yield outgassing data within the dynamic range of the test apparatus. Sample mass is determined on a laboratory balance to an accuracy of ± 10 μ gram.

TEST PROCEDURE

As mentioned previously, there are two versions of the test method. Test Method A prescribes specific QCM and sample temperatures and Test Method B allows for variances in these parameters to permit the user to customize a test to acquire application-specific data. Variations related to test operation under Test Method B must be noted in order to accurately interpret the data. Except for effusion cell and QCM setpoint temperatures the actual test procedure is the same for Test Method A or B.

Test Chamber Preparation

In preparation for outgassing measurements the main test chamber is evacuated to less than 5×10^{-5} torr and the cryogenic heat sinks for the QCMs and shrouds are then activated. The QCMs are heated to 398 K to remove any residual contaminants by evaporation and then allowed to cool to their operating

temperatures. The interlock chamber containing the effusion cell is also evacuated to less than 5×10^{-5} torr at this time. These preceding steps are performed only when the apparatus is first turned on. For a series of outgassing measurements (i.e. normal operation) the chamber remains evacuated with the cryogenic heatsinks on and the QCMs at their operating temperatures. This is good practice for maintaining the cleanest apparatus with low background.

Effusion Cell and Sample Preparation

Prior to a test the effusion cell is solvent cleaned and vacuum baked at 398 K for at least 12 hours in the interlock chamber. The cell is then cooled to ambient temperature, the interlock chamber is raised to one atmosphere using dry nitrogen, and the cell is removed for sample insertion. The interlock chamber is purged with dry nitrogen gas during the entire time it is at one atmosphere to minimize adsorption of water vapor. The sample is placed in the cleaned effusion cell, and the cell is placed on its holder in the interlock chamber. The interlock chamber is then closed to the atmosphere and the nitrogen gas purge is stopped.

Isothermal Outgassing Test

At the beginning of a test the main chamber is at stable vacuum (about 1×10^{-9} torr for the Lockheed apparatus) with heat sinks and shrouds cold, and the QCMs are at their operating temperatures with their output frequencies at equilibrium. For Test Method A the temperatures for the three QCMs are specified to be ≤ 90 K, 160 K and 298 K and each stable within ± 0.5 K. The coldest QCM on the Lockheed apparatus is actually at about 80 K. The ASTM standard defines QCM frequency equilibrium as when the frequencies of each QCM vary by less than 0.2 Hz/minute when averaged over a 20 minute period.

Acquisition of QCM frequencies and temperatures, and effusion cell temperature is initiated about 20 minutes before the beginning of interlock chamber evacuation. This 20 minutes allows for verification of the stability of QCM frequencies and temperatures. Data is collected at 5 or 10 minute intervals with time zero being defined as the beginning of the interlock chamber evacuation.

The test begins with initiation of evacuation of the interlock chamber containing the effusion cell from atmospheric pressure. The ASTM procedure specifies that the interlock chamber containing an empty effusion cell should be capable of reaching 1×10^{-5} torr in 5 minutes. After 5 minutes of pumping the isolation valve between the main chamber and the interlock chamber is opened for effusion cell insertion into the main chamber. Selection of the 5 minute initial evacuation is a compromise between the desire to reduce the interlock chamber pressure as much as possible before opening the isolation valve to minimize the ensuing rise in main chamber pressure, and the desire to obtain data as soon as possible after the sample has been first exposed to vacuum. During non-standard testing at Lockheed the interlock chamber evacuation period has been as short as 1 minute.

When the effusion cell has been positioned on its holder in the main test chamber the cell is heated to the specified test temperature. Test Method A specifies that each material sample shall be tested at three temperatures. The first test is at 398 K and the second test is at 348 K. A third test is conducted at 323 K or 373 K depending on the contaminant deposition on the ≤ 90 K QCM during the previous two tests. If the ≤ 90 K QCM deposition from the 348 K sample test is less than 5 percent of that from the 398 K sample test then the third test is conducted at 373 K. Effusion cell temperature is controlled to within ± 0.5 K of the specified value. Sample temperature is probably the most application specific parameter involved in outgassing characterization tests and is therefore the most common test method variation. Outgassing measurements have been performed at Lockheed for sample temperatures ranging from 130 K to 450 K.

The isothermal outgassing test continues for up to 5 days for each sample. The test can be terminated before 5 days if the mass deposition rate on the ≤ 90 K QCM is less than twice that of the background deposition rate. The background deposition rate is determined by running a blank outgassing test on an empty effusion cell. ASTM E 1559 specifies that the background deposition rate on the ≤ 90 K QCM due to an empty effusion cell should be less than 5×10^{-13} g/cm² s. For a 10 MHz QCM this

corresponds to a frequency shift of about 10 Hz/day. With careful apparatus design and construction, Lockheed has been able to achieve background deposition rates on its 80 K QCM of about 2 Hz/day.

An isothermal outgassing test also should be terminated if the deposit mass on a QCM gets large enough to cause inaccuracies in the output signal. Too large a deposit will damp out the oscillating crystal and large deposits (particularly liquids) may also not be coupled appropriately to the crystal. The point at which inaccuracies due to deposit size become significant may vary depending on the QCM and nature of the collected deposit. The ASTM standard specifies that if a QCM deposit exceeds 2×10^{-4} g/cm² the test should be terminated. For a 10 MHz QCM this corresponds to a frequency shift of about 45 KHz.

At the end of the isothermal outgassing test period, the effusion cell is removed from the main chamber via the interlock, the interlock chamber is repressurized with dry nitrogen gas, and the effusion cell is allowed to re-equilibrate to ambient temperature. Once the cell is within 10 K of ambient room temperature it is removed from the interlock chamber, and the sample is removed from the cell and reweighed on the laboratory balance. Before starting another isothermal outgassing test, the effusion cell is thoroughly solvent cleaned and vacuum baked at 398 K for at least 12 hours. This effusion cell preparation for the next test is easily accomplished in the interlock chamber while the subsequent QCM thermogravimetric analysis test is being performed.

QCM Thermogravimetric Analysis Test

At the end of the isothermal test the deposits collected on the QCMs are subjected, in turn, to QCM thermogravimetric analysis (QTGA). This test measures the QCM deposit mass as a function of temperature. Each QCM is heated from its base operating temperature to 398 K. Because the frequency of a QCM crystal is sensitive to heat flux through the crystal, the heating rate must be low enough to keep heat flux-induced frequency changes within acceptable limits. The heating rate selected for the ASTM procedure is 1 K/minute, based on published studies of heat flux effects on QCM frequency⁵. A maximum temperature of 398 K is selected for QTGA because this is equal to the maximum sample temperature and all deposited outgassed species should evaporate at temperatures below this unless they have changed chemically since deposition. It is also the maximum operating temperature of the QCMs.

After reaching 398 K, a QCM is maintained at this temperature until its frequency becomes stable i.e. until its collected deposit has completely reevaporated. The QCM is then cooled back to its operating temperature in preparation for the next isothermal outgassing test.

Because the reevaporation of collected species off a QCM can be a rather fast and eventful process compared to the outgassing test, the QCM temperature and frequency are recorded at one minute intervals during QCM thermogravimetric analysis .

DATA PROCESSING

The ASTM E 1559 test method generates material data from *ex situ* and *in situ* measurements. The *ex situ* measurements consist of the pre- and post-test weighing of the sample on a laboratory balance. The *in situ* measurements consist of isothermal outgassing test data and QCM thermogravimetric analysis data. The *ex situ* laboratory balance measurements are reduced to yield an *ex situ* Total Mass Loss, TML_{ex} , value. The QCM frequency data from the isothermal outgassing test are reduced to give *in situ* Total Mass Loss, TML , and Volatile Condensable Material, VCM , as functions of test time. The QCM frequency and temperature data from the QCM thermogravimetric analysis are converted to mass remaining on the QCM, m_Q , as a function of QCM temperature.

In addition to this data processing specified by ASTM E 1559, the measured QCM data also can also analyzed to provide outgassing rates from the sample during the isothermal outgassing test and evaporation rates from the QCM during QCM thermogravimetric analysis. This data reduction will be discussed below in order to illustrate the scope of material characterization information that is generated by this test method.

Ex Situ Measurements

The *ex situ* Total Mass Loss, TML_{ex} , in percent is calculated from pre- and post-test laboratory balance weighings by the following equation:

$$TML_{ex} = 100 * \left[\frac{m_{s+h}(i) - m_{s+h}(f)}{m_{s+h}(i) - m_h} \right] \quad (1)$$

where m indicates a measured mass, the subscripts s and h indicate the sample and holder, and i and f indicate initial and final weighings, respectively.

Isothermal Outgassing Test

The pertinent data acquired during the isothermal outgassing test are the frequencies of the QCMs and the time since the start of the evacuation of the effusion cell in the interlock chamber. Isothermal outgassing data are calculated from QCM frequency data using the QCM mass sensitivity and the view factor from the QCM to the effusion cell orifice.

The QCM mass sensitivity is used to convert the QCMs output frequency into units of mass deposited on the QCM. The mass deposited on a QCM is calculated from the following equation:

$$m_d(T_q, T_s, t) = K_s [f(T_q, T_s, t) - f(T_q, T_s, 0)] \quad (2)$$

where $m_d(T_q, T_s, t)$ is the mass deposit density (g/cm^2), $f(T_q, T_s, t)$ is the frequency (Hz) of the QCM at temperature T_q with the sample at temperature T_s at time t , and K_s is the mass sensitivity factor ($\text{g}/\text{cm}^2 \text{ Hz}$). Since the relationship between frequency shifts and mass deposited on the QCM crystal is linear well beyond the operating regime of the ASTM E 1559 measurements, the mass sensitivity factor, K_s , is constant for a given QCM type. The ASTM E 1559 standard provides K_s values for typical QCMs. The QCMs used in the Lockheed apparatus have a sensitivity of, $K_s = 4.49 \times 10^{-9} \text{ g}/\text{cm}^2 \text{ Hz}$. Further discussion on mass sensitivity of QCMs can be found in reference 5.

The second principal piece of information required for analyzing the isothermal outgassing test data is the view factor from the QCM to the effusion cell orifice. This view factor relates the mass deposit on the QCM to the mass lost from the sample and can be calculated from the following equation:

$$F_q = \frac{\pi r^2 W_{L/R}}{B(\phi_1) \cos(\phi_1) \cos(\phi_2)} \quad (3)$$

where

- F_q = the view factor for QCM_q to the effusion cell orifice (cm^2)
- r = the distance from the cell orifice to the QCM_q crystal (cm)
- ϕ_1 = the angle between the QCM_q-to-orifice line of sight and the orifice normal
- ϕ_2 = the angle between the QCM_q-to-orifice line of sight and the QCM_q normal
- L = the length of the effusion cell orifice (mm)
- R = the radius of the effusion cell orifice (mm)
- $B(\phi_1)$ = the directivity of the angular flow from the effusion cell orifice
- $W_{L/R}$ = the transmission probability of the orifice

The $B(\phi_1)$ and $W_{L/R}$ functions account for the deviation from a cosine distribution for molecular flow leaving an orifice of finite length. The angular flow directivity, $B(\phi_1)$, can be calculated from the following equations⁶:

$$B(\phi_1) = 1 - \frac{2}{\pi}(1 - \gamma) \left[\arcsin(p) + p\sqrt{1 - p^2} \right] + \frac{4}{3\pi}(1 - 2\gamma) \frac{1 - (1 - p^2)^{3/2}}{p} \quad \text{for } p \leq 1 \quad (4)$$

and

$$B(\phi_1) = \gamma + \frac{4}{3\pi} \frac{(1 - 2\gamma)}{p} \quad \text{for } p > 1 \quad (5)$$

where

$$p = \frac{L \tan(\phi_1)}{2R} \quad (6)$$

and

$$\gamma = \frac{\sqrt{L^2 + 4R^2} - L}{2R + \frac{4R^2}{\sqrt{L^2 + 4R^2}}} \quad (7)$$

The other flux distribution related function in Equation 3 that needs to be established is the transmission probability, $W_{L/R}$. This factor represents the fraction of molecules entering the upstream face of the effusion cell orifice which exit the downstream face towards the QCMs. $W_{L/R}$ is a complex function of the geometry and dimensions of the orifice. Calculated values are available in literature^{7,8} and are briefly summarized in the ASTM E 1559 standard.

The effusion cell orifice dimensions and geometries of the Lockheed apparatus are fully compliant with Test Method A. An effusion cell with an orifice that is 3.0 mm long by 3.0 mm diameter is positioned 15 cm from the face of the QCMs such that all the QCMs have the same view factor to the orifice and $\phi_1 = 10^\circ$ and $\phi_2 = 0^\circ$. Using Eqs. 4 through 7 and References 7 and 8 we find that these parameters result in a flux distribution where $B(\phi_1) = 0.8881$ and $W_{L/R} = 0.5136$. Substitution of these values into Equation 3 gives a value for the QCM-to-cell orifice view factor of $F_q = 415.08 \text{ cm}^2$.

Total Mass Loss

The *in situ* Total Mass Loss (TML) expressed in percent of sample mass is calculated from the mass density deposited on the $\leq 90 \text{ K}$ QCM and normalized with respect to the initial mass of the sample using the following equation:

$$TML(T_s, t) = 100 * \left[\frac{F_1 m_d(T_1, T_s, t)}{m_{s+h}(i) - m_h} \right] \quad (8)$$

Equation 8 assumes that all of the outgassing flux impinging on this QCM is condensed. Some highly volatile outgassed species such as atmospheric gases will not deposit on the QCM but the error introduced by this assumption is acceptably small⁴.

In some cases it is desirable to normalize the total mass loss to some other sample parameter. As an example, for coatings it is sometimes useful to normalize the data with respect to the surface area of the sample. That is, the total mass loss data could be expressed in terms of mass lost from the sample per unit area of sample (g/cm^2). ASTM E 1559 does not provide the specific equations for calculating total mass loss in these units, but the data can be easily reduced once m_d and F_1 are established by substituting the sample surface area, A_s , for the initial sample mass in Equation 8.

Volatile Condensable Material

The Volatile Condensable Material (*VCM*) expressed in percent of sample mass is calculated from the mass density deposited on the higher temperature QCMs and normalized with respect to the initial mass of the sample using the following equation:

$$VCM(T_q, T_s, t) = 100 * \left[\frac{F_q m_d(T_q, T_s, t)}{m_{s+h}(i) - m_h} \right] \quad (9)$$

where q corresponds to the higher temperature QCMs. As with the total mass loss data reduction mentioned above, *VCM* can be expressed in alternative units by making the appropriate substitutions into Equation 9.

Outgassing Rate

A specific data reduction technique is not provided by ASTM E 1559 for calculating material outgassing rates. However, the test method does provide all the necessary raw data so that the end user can perform this analysis. The total outgassing rates from the sample are calculated from the data from the ≤ 90 K QCM. As with the TML calculations, this analysis assumes that essentially all of the outgassing flux impinging on the ≤ 90 K QCM is condensed. The mass deposit density on the ≤ 90 K QCM, $m_d(T_1, T_s, t)$, is differentiated as a function of time to give the deposition rate on this QCM. This deposition rate, $\dot{m}_d(T_1, T_s, t)$, is then used with the QCM-to-cell orifice view factor, F_q , and the sample surface area, A_s , in the following equation to calculate the total outgassing rate from the sample, $OGR(T_s, t)$, in units of $g/cm^2 s$:

$$OGR(T_s, t) = \frac{F_1 \dot{m}_d(T_1, T_s, t)}{A_s} \quad (10)$$

QCM Thermogravimetric Analysis

The pertinent raw data acquired during the QCM thermogravimetric analysis consist of the frequencies and temperatures of the QCMs. The time between data measurements from the QCMs can be used for optional evaporation rate analysis.

Mass Loss from the QCM

As a QCM is heated up from its base operating temperature, the deposit collected during the isothermal outgassing test evaporates from the crystal. This causes a decrease in the QCMs output beat frequency. These frequency data are used with Equation 11 to calculate the mass loss (g/cm^2) from the QCM deposit during QTGA, $m_Q(T_q, t)$, as a function of temperature for each of the QCMs.

$$m_Q(T_q, t) = K_s [f(T_q, 0) - f(T_q, t)] \quad (11)$$

Although the types of QCMs specified for use in ASTM E 1559 utilize a reference crystal which helps compensate for thermal drift of the QCM frequency, some temperature effects on the output will still be present during the thermogravimetric analysis. Methods for correcting for this frequency-temperature response of a QCM have not been specified by ASTM E 1559. Lockheed, however, obtains a frequency-temperature response curve for a clean QCM by subjecting it to the QTGA heating profile of 1 K/minute. This clean QCM frequency-temperature profile (or a curve fit to it) can be then subtracted from the QCM thermogravimetric analysis test data as a correction.

Evaporation Rate from the QCM

More insight into the number of different species leaving the collected deposit during QCM thermogravimetric analysis and information about their vapor pressures can be obtained by examining the evaporation rates of the species from the QCMs. While, ASTM E 1559 does not specify a data reduction technique for calculating the evaporation rates from a QCM, the rates can be obtained by differentiating the QTGA mass loss data, $m_Q(T_q, t)$, from Equation 11 and taking into account the transmission probability of the aperture in the QCM case through which the evaporating flux leaves from the crystal. The evaporation rate from a QCM ($\text{g}/\text{cm}^2 \text{ s}$) is calculated from the following equation:

$$\text{Evaporation Rate from QCM} = \frac{\dot{m}_Q(T_q, t)}{W_q} \quad (12)$$

where W_q is the transmission probability for the aperture in the QCM case. This transmission probability is a function of the geometry of the aperture and can be obtained from references 7 and 8. $W_q = 0.89$ for the QCMs used in the Lockheed apparatus.

DATA EXAMPLE

Results from a typical test are presented below to illustrate the material contamination characterization data provided by the ASTM E 1559 test. The test standard specifies a standard format of tabulated data which facilitates electronic transmittal and archiving of the data. For illustrative purposes all of the proceeding data is presented in a graphical format.

Material Sample

The material used for this example is Chemglaze Z306 paint, a material commonly used in vacuum applications because of its optical properties. Because of its extensive use by industry, this paint has been tested in a variety of configurations. The data from this test was acquired in support of the evaluation of a new primer.

The material consists of a one-component, flat-black coating with carbon black pigment and polyurethane binder manufactured by Lord Corporation. The primer is produced by Deft Chemical Coatings. The sample consisted of two aluminum foil discs sprayed on one side with Deft primer and Chemglaze Z306. Sample dimensions and weights were obtained throughout the painting process. These data are summarized below in Table 1.

Table 1 Chemglaze Z306/Deft Primer Samples

	Diameter (cm)	Primer Thickness (cm)	Topcoat Thickness (cm)	Substrate Mass (g)	Primer Mass (g)	Topcoat Mass (g)	Total Coating Mass (g)
Disc #1	4.12	0.0013	0.0081	0.16601	0.02392	0.10227	0.12619
Disc #2	4.12	0.0013	0.0084	0.16623	0.02475	0.10566	0.13041
				Totals	0.04867	0.20793	0.25660

The dimensions of the discs give a total sample area of 26.66 cm^2 . The sample discs were positioned in the effusion cell so that outgassing from the painted faces was not impeded.

Isothermal Outgassing Test

The isothermal outgassing test was performed per ASTM E 1559 Test Method B since four QCMs with gold electrodes were used. The QCMs were maintained at 80 K, 160 K, 220 K and 298 K. The material sample was at 125°C for a test duration of 24 hours. A post-test weighing of the sample was not made so an *ex situ* TML value was not obtained for this sample.

Figure 3 shows the actual frequency shift on the 80 K QCM and the corresponding mass deposit density (Equation 2) as functions of the test time. This is a typical curve for mass accumulation on a QCM showing a monotonically increasing deposit. At the start of the test (test time = 0) the clean QCM base frequency was about 2768 Hz. This increased by about 1759 Hz over the duration of the test, corresponding to a net deposit on the crystal of about $7.9 \times 10^{-6} \text{ g/cm}^2$.

Figure 4 gives the TML for the sample as a function of time. These data are obtained by applying Equation 8 to the 80 K QCM mass deposit density data of Figure 3. The $7.9 \times 10^{-6} \text{ g/cm}^2$ deposited on the QCM corresponds to a TML of 1.277 percent from the sample. Figure 4 also gives the TML data in units of g/cm^2 in which the mass loss is normalized with respect to the 26.66 cm^2 surface area of the sample. The TML for the sample in these units was $1.229 \times 10^{-4} \text{ g/cm}^2$.

In order to keep the data presentation concise, the frequency and mass deposit density data are not presented here for the warmer collector QCMs at 160 K, 220 K, and 298 K. However, these data were reduced using Equation 9 to obtain the VCM data shown in Figure 5. As with the TML data, this figure gives the VCM data in units of percent and g/cm^2 . Figure 5 shows that as the collector QCM temperatures increase the VCM decreases, since the higher volatility species are not able to condense on the warmer QCMs. The VCM for the 298 K QCM shows a maximum after about 7 hours then a subsequent decrease. The deposition on a QCM is the kinetic balance between the total impingement flux and the reevaporation flux of higher volatility species. The constant evaporation rate of a species from the 298 K QCM is temporarily (for the first 7 hours) smaller than the impinging flux of this species from the sample and so a net deposition of the species on the QCM occurs. As this species is depleted from the sample its outgassing contribution to the impingement flux on the QCM is less and at 7 hours the kinetic balance is shifted such that the evaporation rate of the species is larger. This species continues to gradually evaporate from the 298 K QCM until it has been depleted from the QCM deposit. It appears that this point is reached at a test time of about 20 hours.

The total outgassing rate for the sample is shown in Figure 6. This is calculated from the mass deposition rate on the 80 K QCM using Equation 10. In this example, the deposition rate on the 80 K QCM was obtained by performing a point-by-point numerical differentiation of the mass deposit data shown in Figure 3. The outgassing rate for the Chemglaze Z306 sample decreases by three orders of magnitude from 10^{-7} to $10^{-10} \text{ g/cm}^2 \text{ s}$ over the 24 hour test.

QCM Thermogravimetric Analysis

At the conclusion of the isothermal outgassing test, QTGA was performed per the ASTM standard. Each of the QCMs was heated from its base temperature to 398 K at 1 K/minute. Only the data from the 80 K QCM are presented here, since this QCM accumulates a deposit containing all the species representative of the outgassing flux.

As the QCM is heated the deposit evaporates from the crystal and the QCM frequency decreases. Figure 7 shows the frequency decrease as a function of QCM temperature for the QCM which was at 80 K during the isothermal outgassing test. As was mentioned previously, it is Lockheed practice to subtract the frequency-temperature response for the clean QCM from the measured output signal obtained during the QTGA of a collected deposit. Therefore, the QTGA data presented here show the QCM frequency decreasing to 0 Hz rather than to its original base frequency of several thousand Hz. Equation 11 is used to reduce the frequency data to obtain the mass loss from the QCM during the QTGA. The results of these

calculations are also presented in Figure 7. Inflection points in Figure 7 reveal when a different species is evaporating from the QCM. The relative amounts of the different species in the QCM deposit can be obtained by comparing the mass loss from the QCM due to each species.

The evaporation of a species from the QCM deposit during QTGA is made more apparent by examining the evaporation rate from the QCM. A point-by-point differentiation of the mass loss from the QCM during QTGA is performed at Lockheed to obtain the rate of mass loss from the QCM. These data are then used with Equation 12 to calculate the evaporation rate from the QCM as a function of QCM temperature. These data for the QTGA of the 80 K QCM are presented in Figure 8. As the temperature of the QCM increases the evaporation rate of a species also increases until it reaches a peak when the amount of that species on the QCM nears depletion. Therefore, the slope of the leading edge of a peak or shoulder in an evaporation rate curve is characteristic of the species being volatilized. The various peaks and different leading edge slopes in Figure 8 indicate at least seven distinct groups of species leaving the QCM. These data provide the basis for establishing additional information on the vapor pressures of these species.

SUMMARY

Material outgassing measurement tests using ASTM E 1559 have been performed in support of various aerospace, electronic and semiconductor oriented companies. These industries are similar in that some of their products operate or are manufactured in a vacuum environment. As the sensitivity of these devices and processes to molecular contamination increases, more detailed characterization of the related construction materials must be obtained.

The ASTM E 1559 test standard is used to characterize the outgassing and deposition kinetics of virtually any material including adhesives, coatings, film and sheet materials, elastomers, composites, and components which can be cut to fit into the effusion cell. Lockheed has also used the test method to measure the vapor pressures of oils and greases. Outgassing rates from 10^{-14} to 10^{-5} g/cm² s and Total Mass Loss from samples of 0.0001 to 5 percent have been measured.

REFERENCES

1. ASTM E 1559, "Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials."
2. ASTM E 595, "Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment."
3. ASTM F 1227, "Standard Test Method for Total Mass Loss of Materials and Condensation of Outgassed Volatiles on Microelectronics-Related Substrates."
4. A.P.M. Glassford and J.W. Garrett, "Characterization of Contamination Generation Characteristics of Satellite Materials," USAF WRDC/MLBT Final Report WRDC-TR-89-4114, 22 November 1989.
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7. P. Clausing, *Z. Phys.*, Vol 66, 1930, pp. 471.
8. S. Dushman, *Scientific Foundations of Vacuum Technique*, 2nd edition, John Wiley and Sons, Inc., New York, 1962, pp. 94.

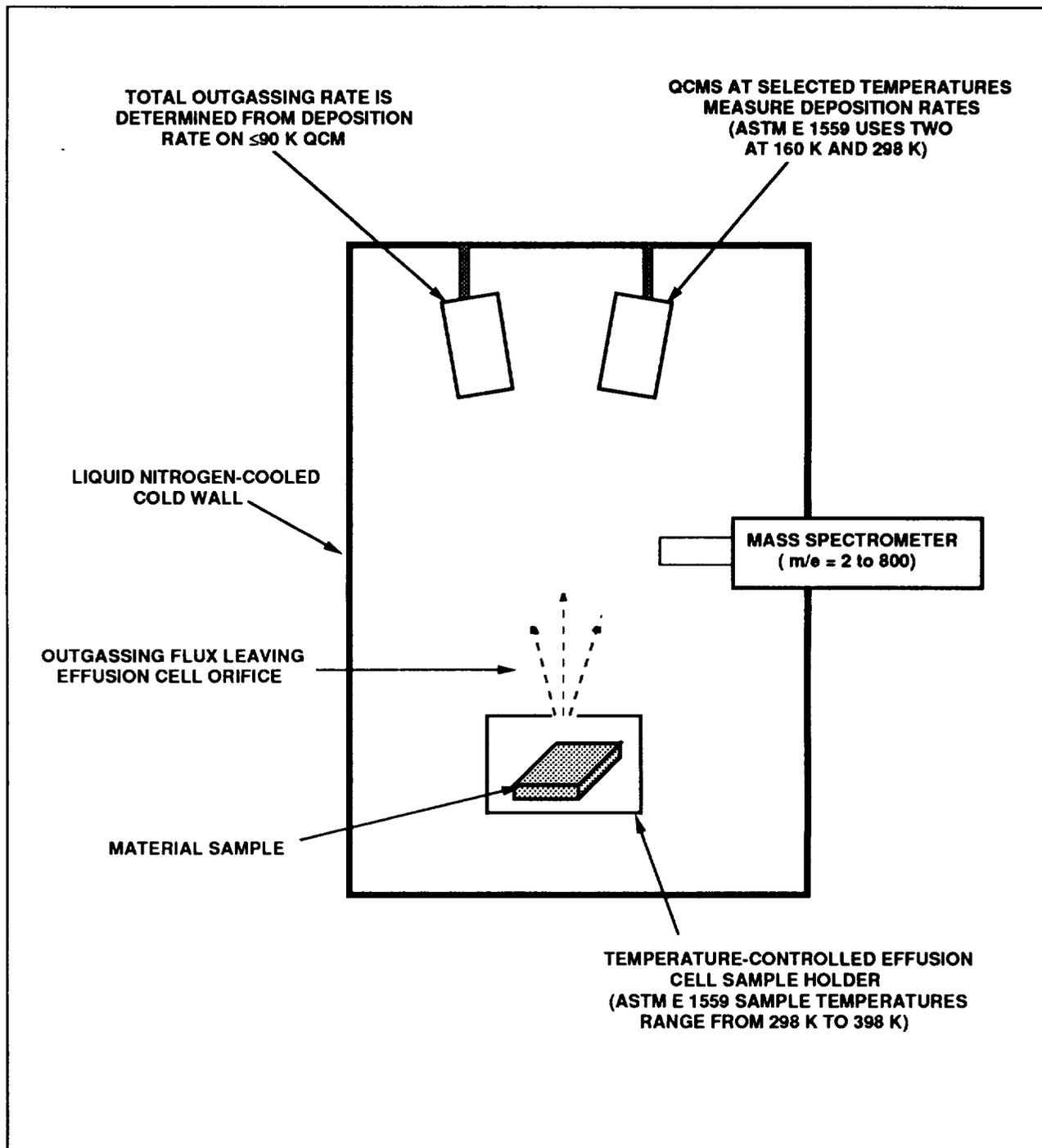


Figure 1. Schematic of the QCM Collection Measurement Method used for ASTM E 1559.

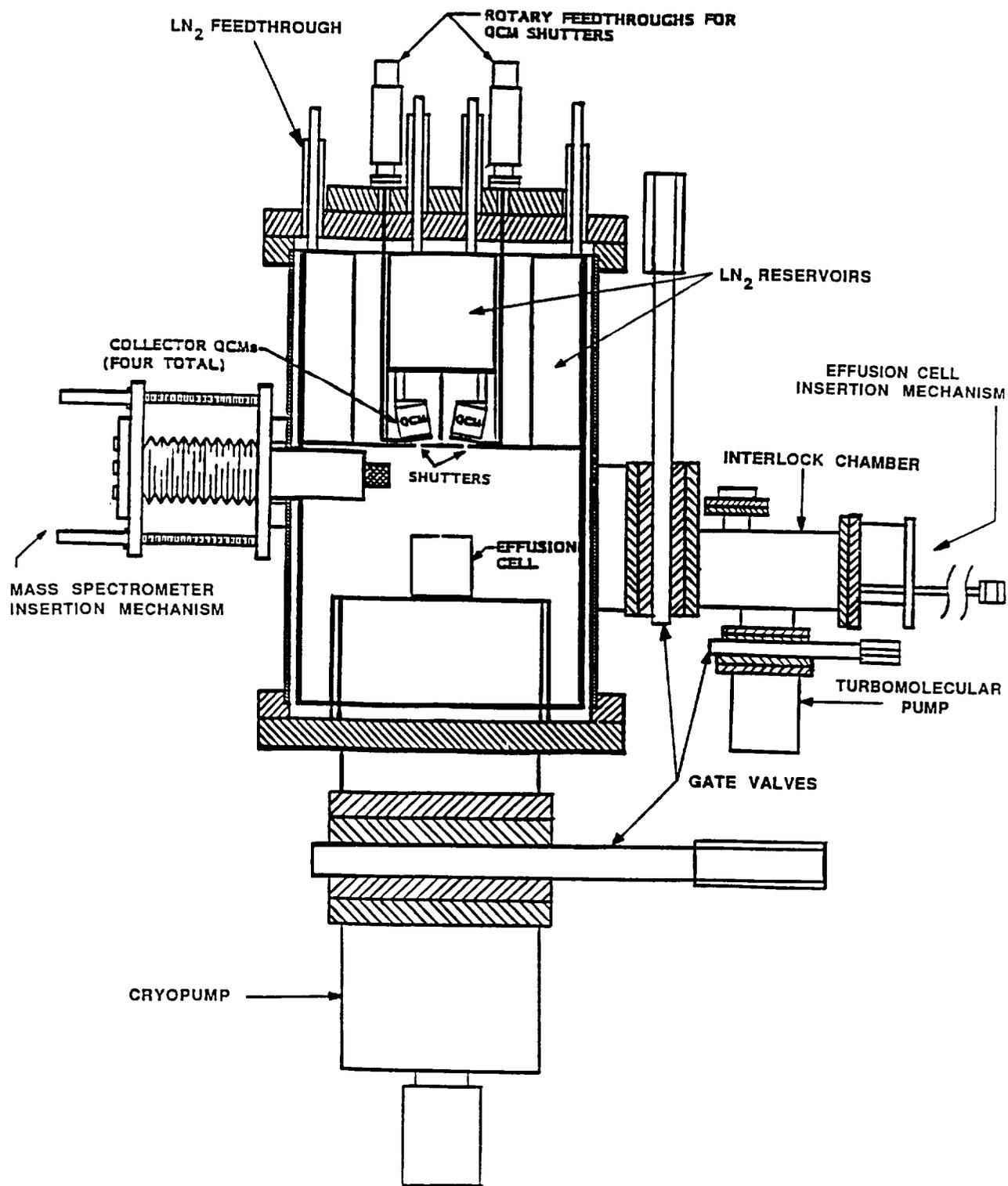


Figure 2. The Lockheed Vacuum Outgassing/Deposition Kinetics Apparatus.

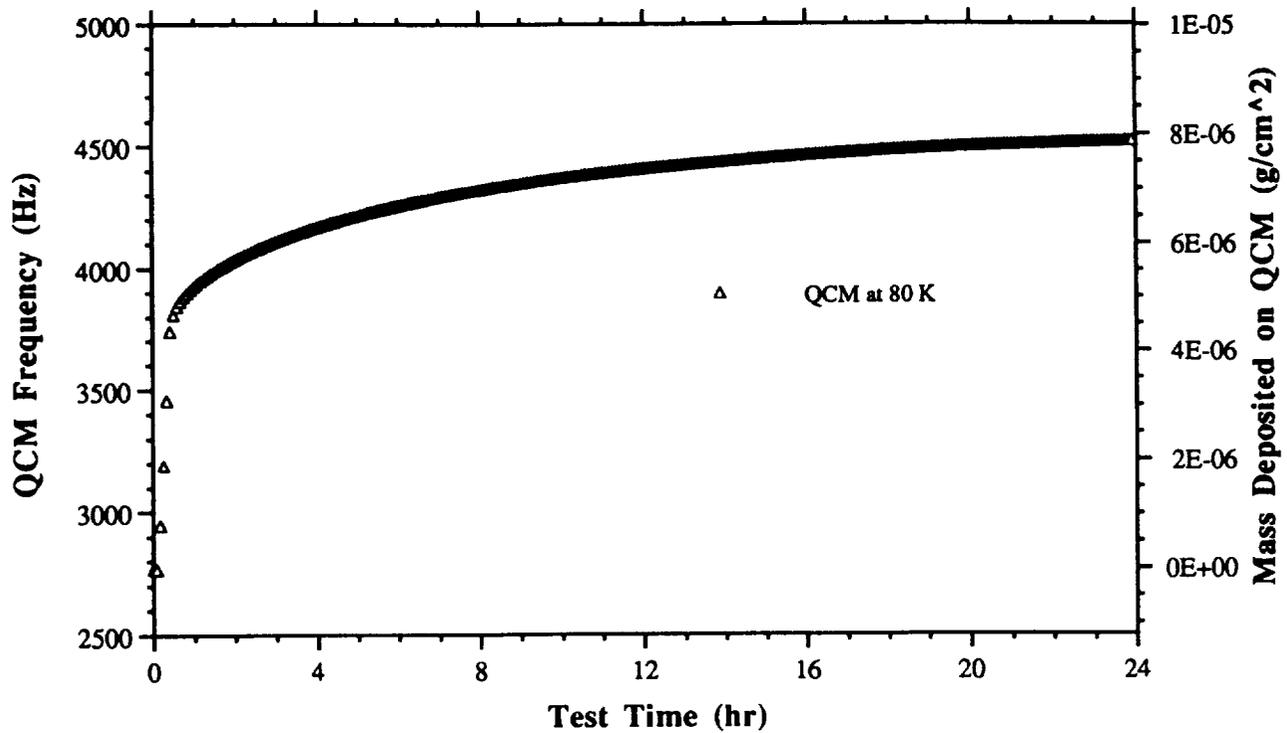


Figure 3. QCM Frequency and Mass Deposited on QCM as a Function of Time for the 80 K QCM during the Isothermal Outgassing Test on Chemglaze Z306/Deft Primer at 125°C.

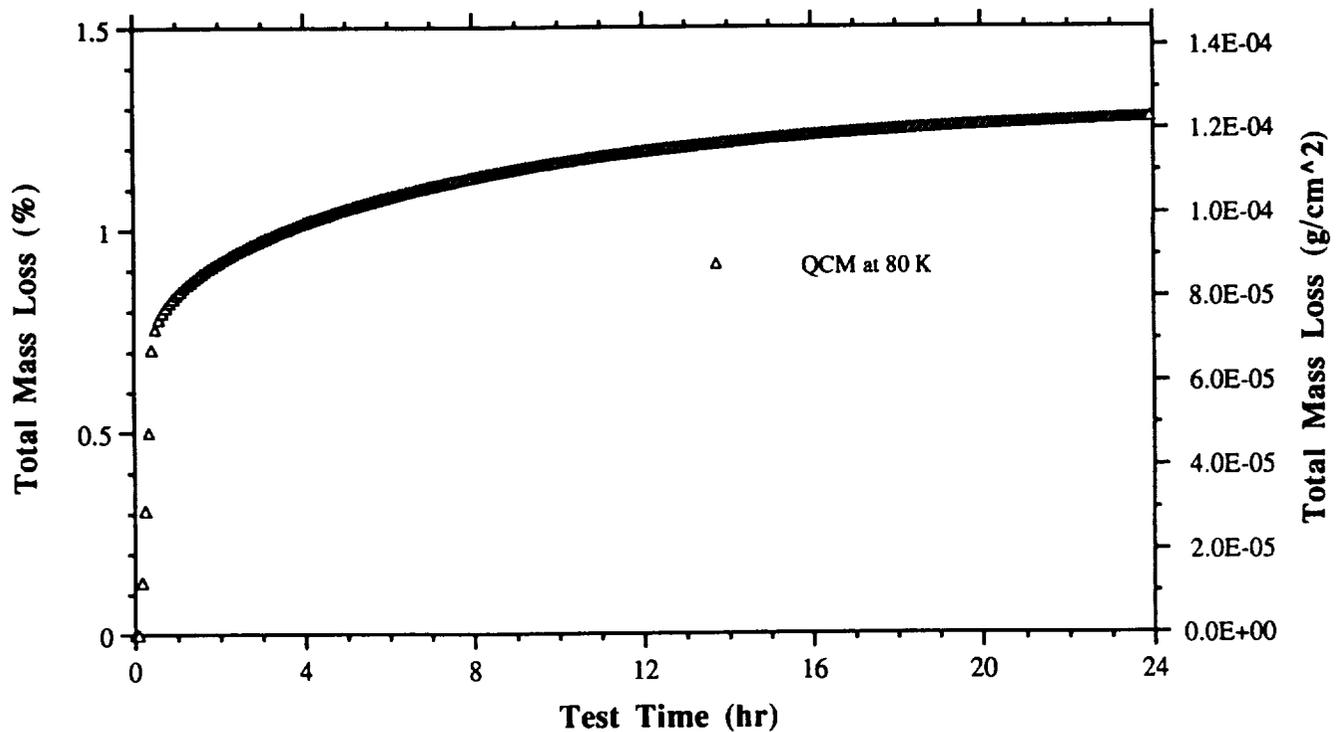


Figure 4. Total Mass Loss from the Sample as a Function of Time during the Isothermal Outgassing Test on Chemglaze Z306/Deft Primer at 125°C.

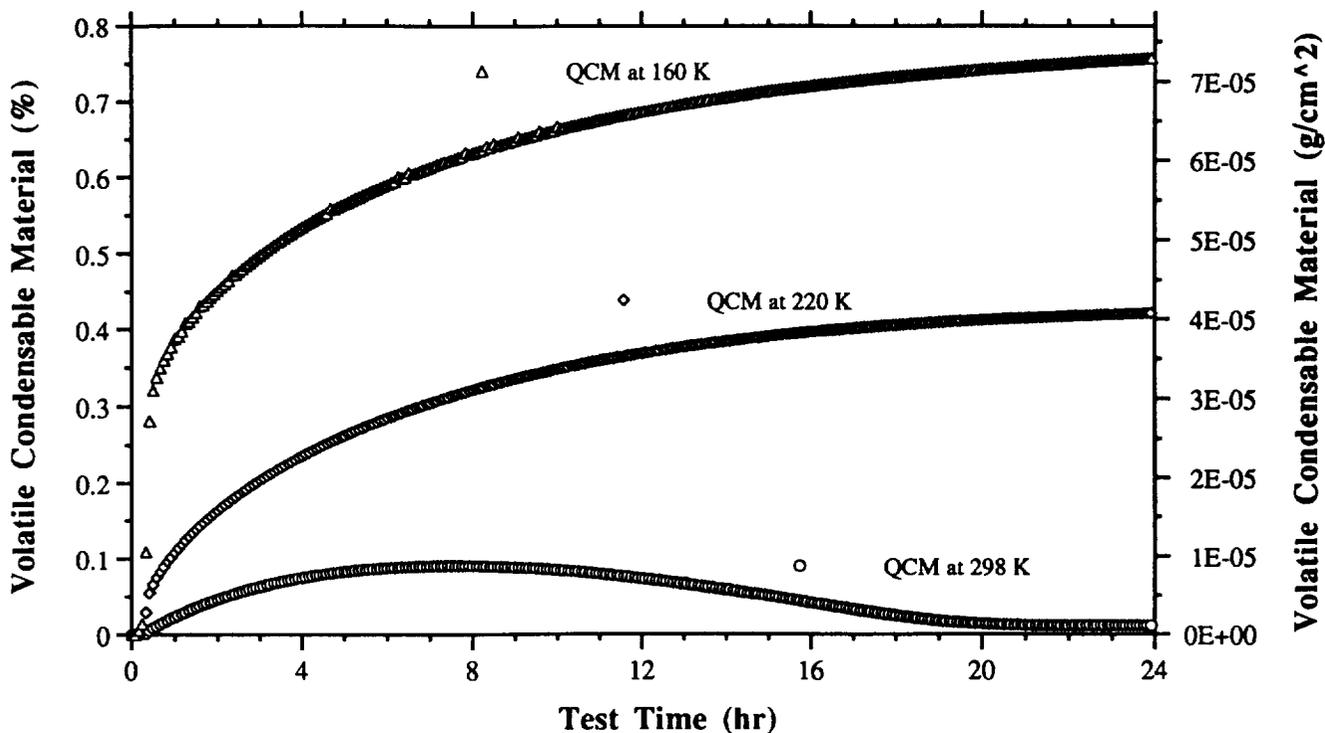


Figure 5. Volatile Condensable Material for QCMs at 160 K, 220 K, and 298 K as a Function of Time during the Isothermal Outgassing Test on Chemglaze Z306/Deft Primer at 125°C.

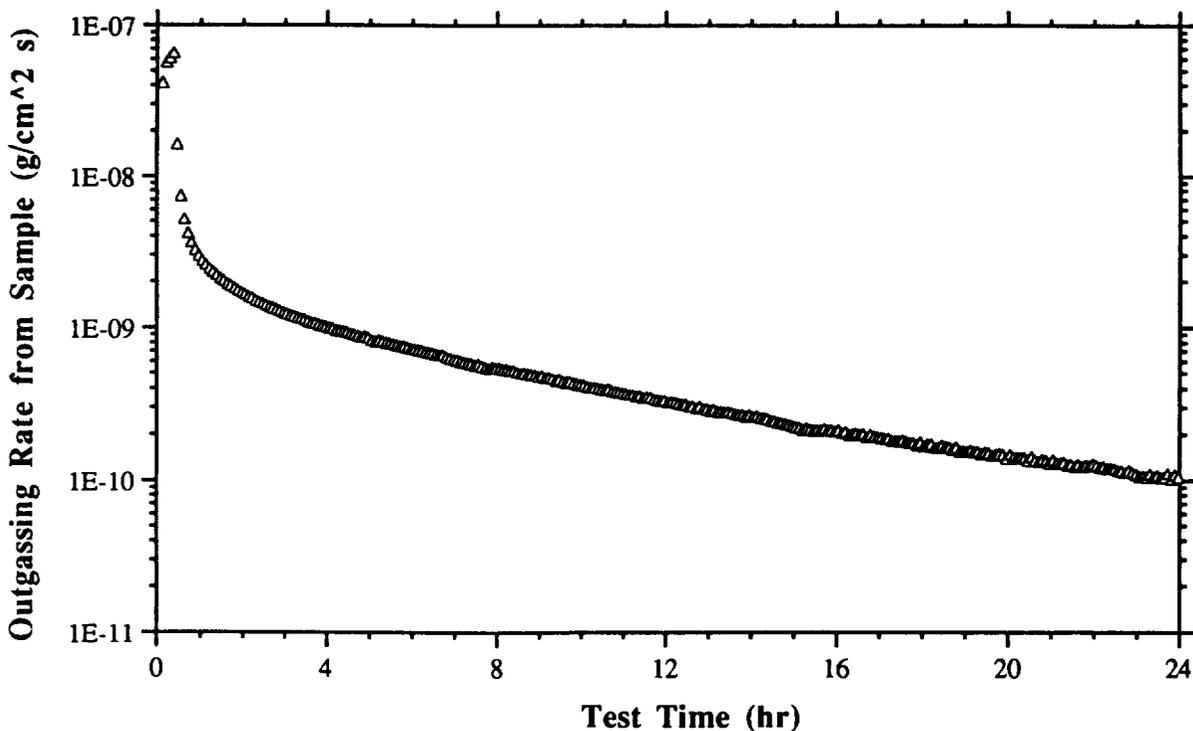


Figure 6. Outgassing Rate from the Sample as a Function of Time during the Isothermal Outgassing Test on Chemglaze Z306/Deft Primer at 125°C.

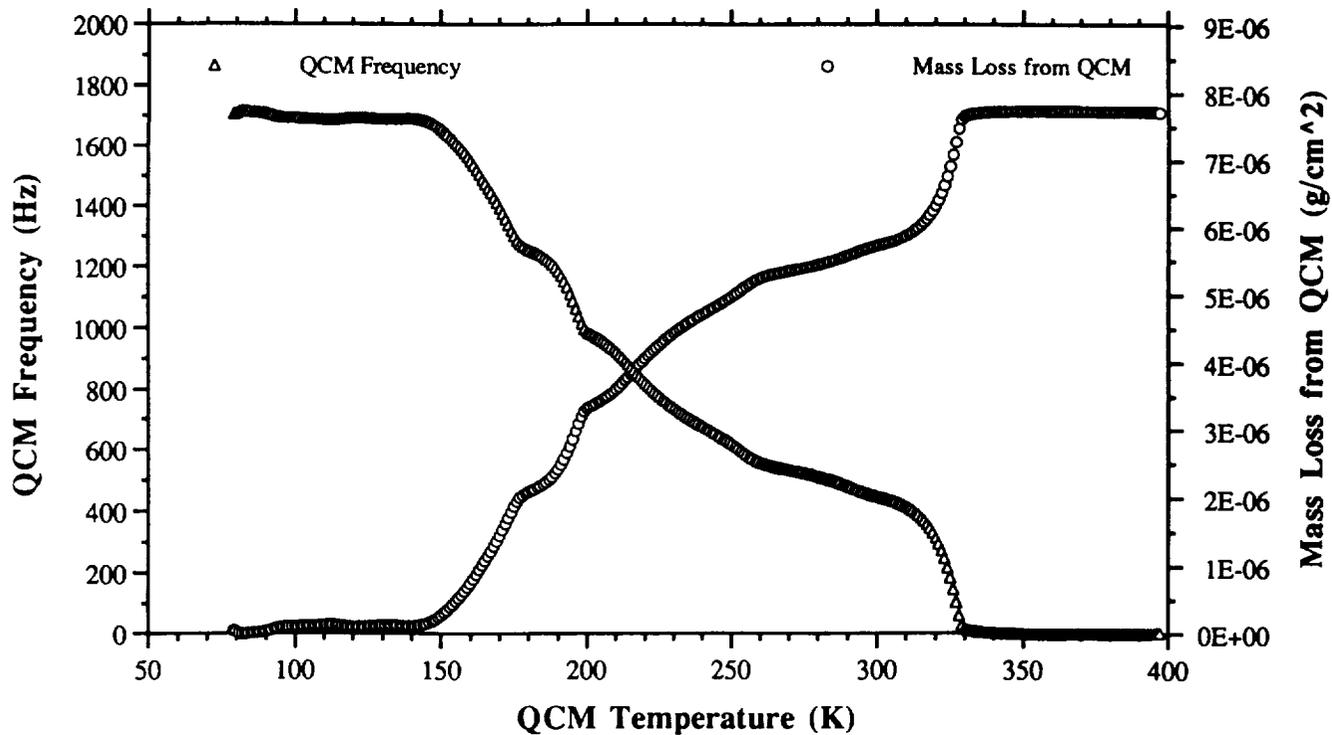


Figure 7. Mass Loss from the 80 K QCM as a Function of QCM Temperature during the QTGA of the Collected Deposit from Chemglaze Z306/Deft Primer at 125°C.

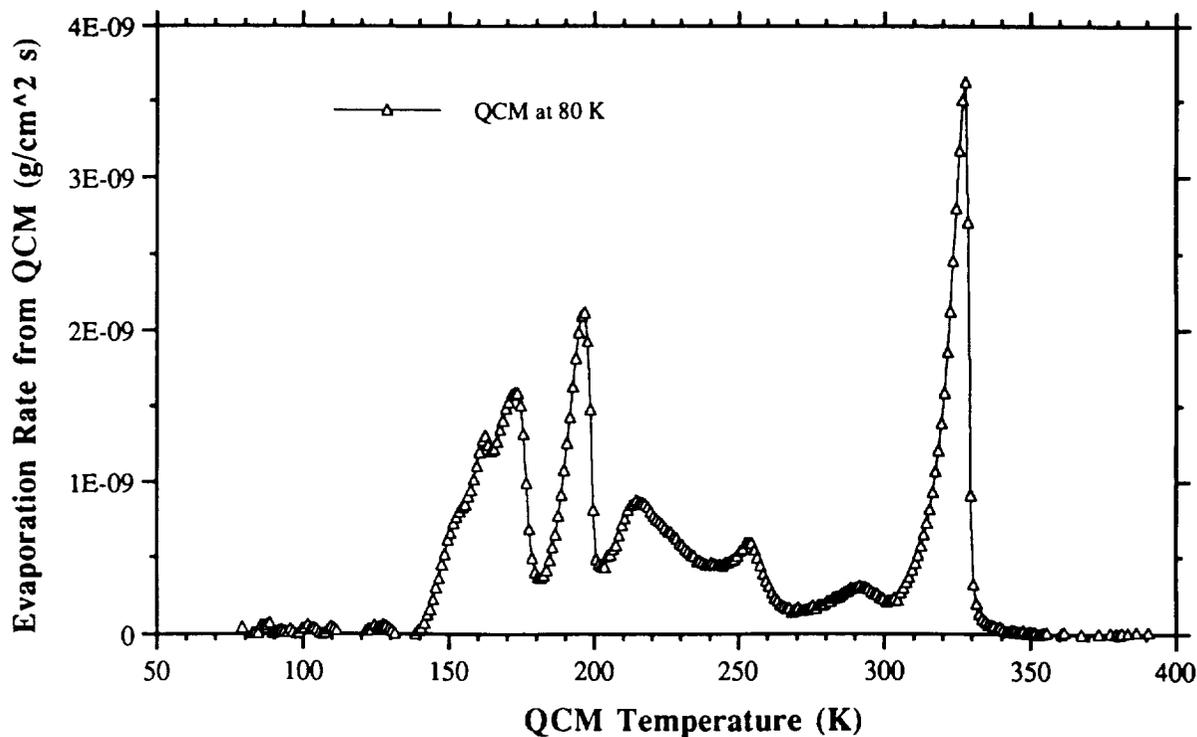


Figure 8. Evaporation Rate from the 80 K QCM as a Function of QCM Temperature during the QTGA of the Collected Deposit from Chemglaze Z306/Deft Primer at 125°C.